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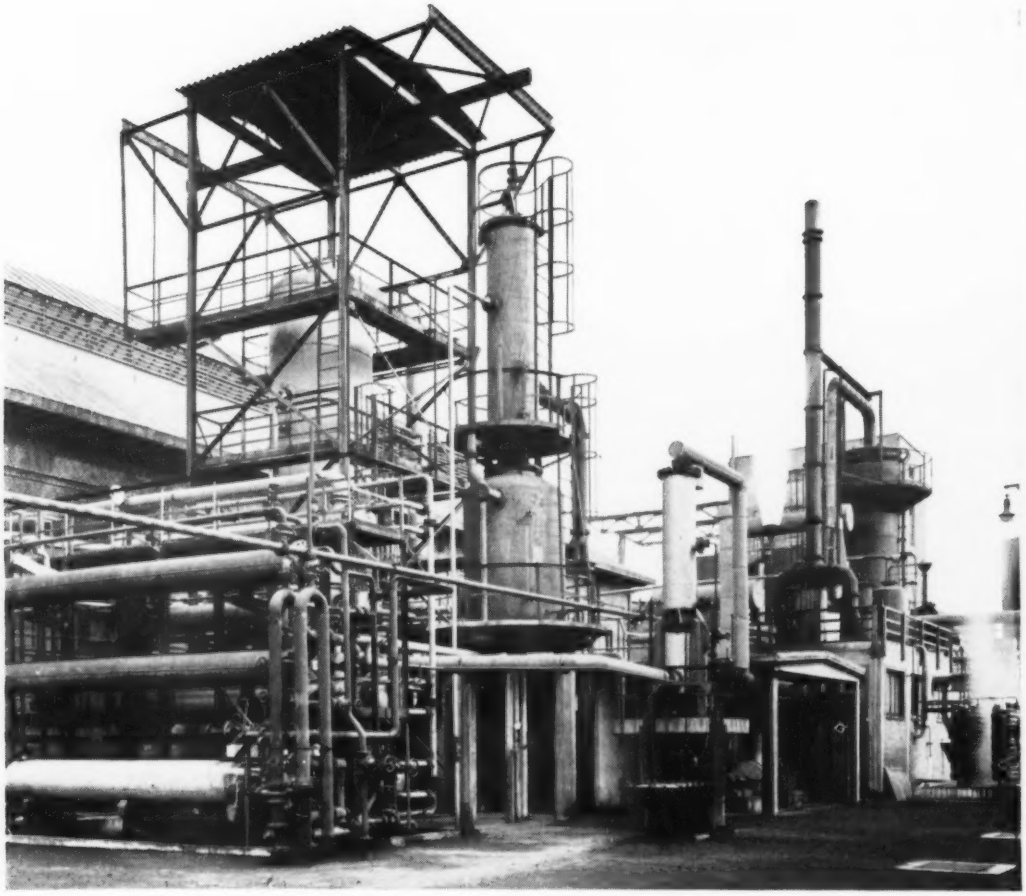
SULPHUR REMOVAL

FROM INDUSTRIAL GASES



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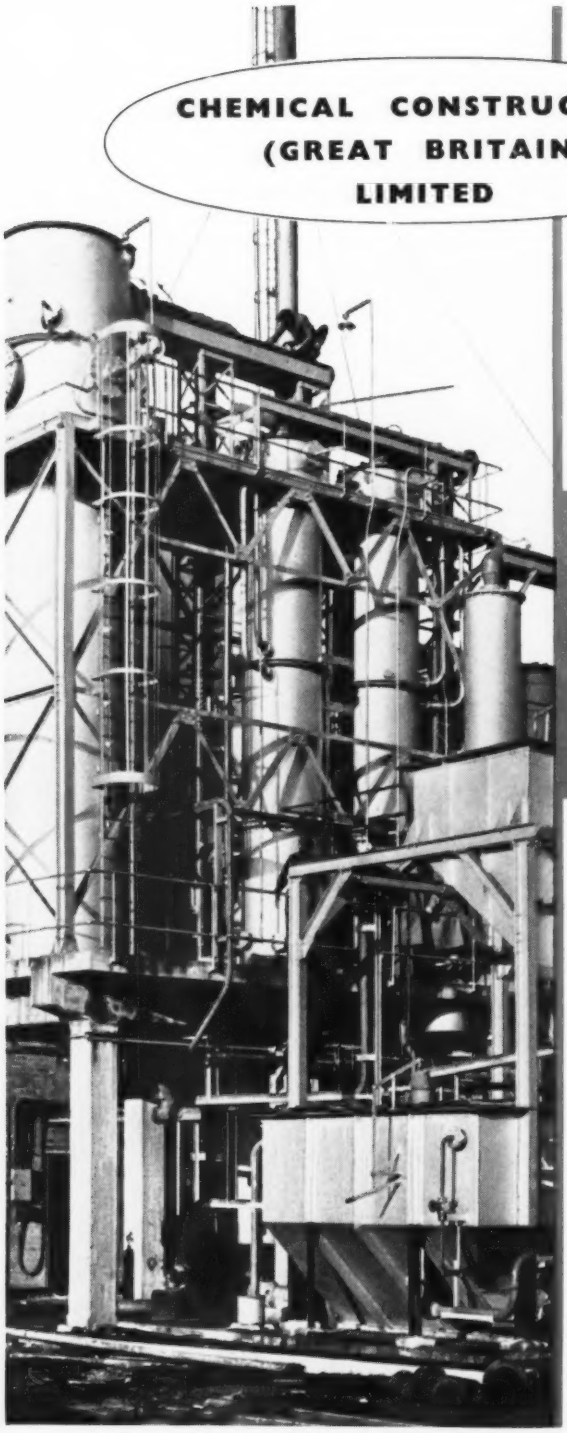

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HEAT RECOVERY IN SULPHURIC ACID MANUFACTURE

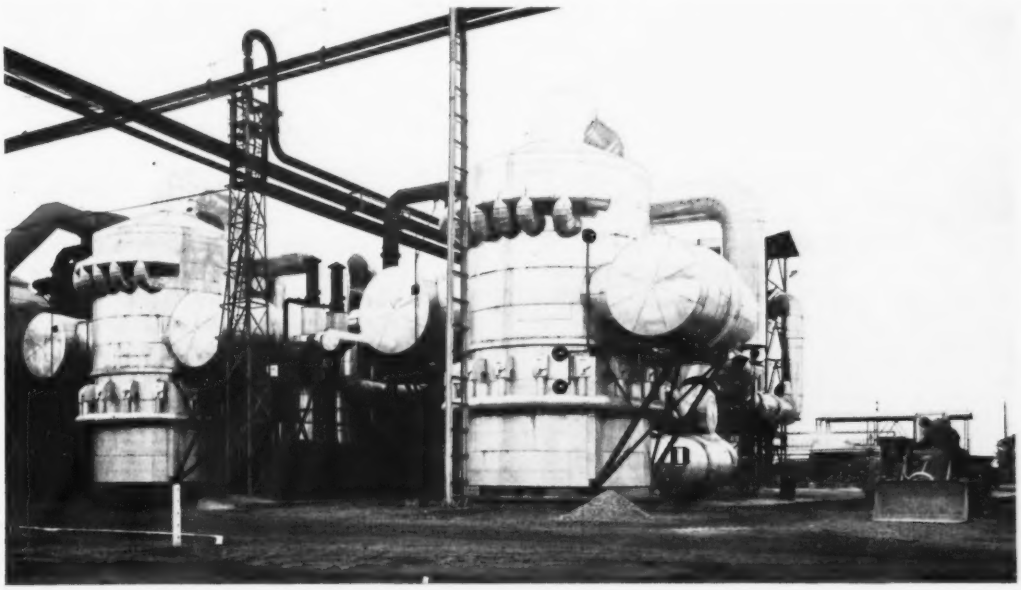
IN EUROPE the manufacture of sulphuric acid has until recently been based mainly on pyrites and most pyrites-burning installations allowed the heat of combustion to be lost. Indeed arrangements were often made to cool the gas sufficiently before its preliminary purification. In brimstone acid plants, however, the greater simplicity of plant and operation established heat recovery sometime ago. The high cost of power has focussed greater attention on this problem and in view of rising competition in the sulphuric acid and allied industries the economics of operation arising from the saving of heat or power are significantly improved.

The Wondelgem Factory of Union Chimique Belge

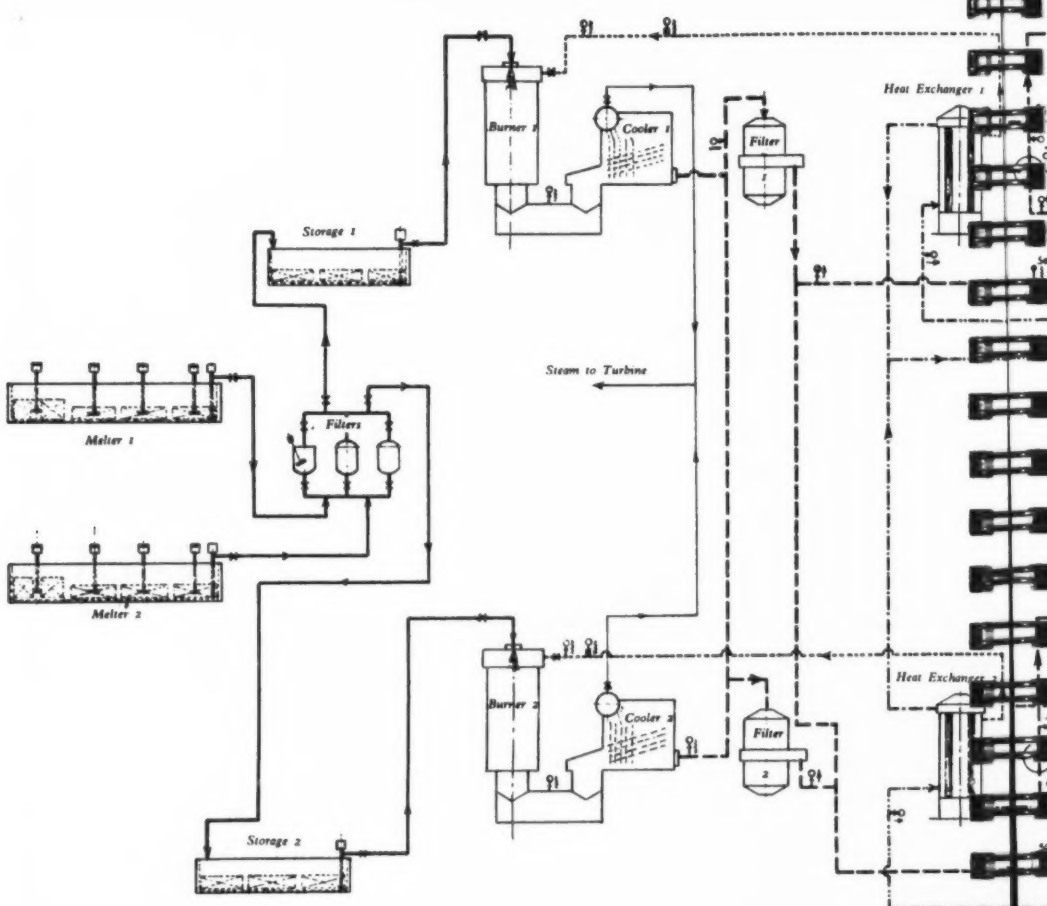
When the brimstone contact acid installation came on stream almost one year ago, the company's aim to make the best possible use of the heat value of sulphur was achieved. The works, mainly occupied in the production of heavy chemicals, had a contact sulphuric acid plant built in 1937, with a capacity of 150 tons a day (100 / H_2SO_4) based on pyrites roasting which was carried out in eight vertical furnaces of conventional type. In 1952, the first stage in the recovery of the heat of combustion of the sulphur was effected by replacing these eight furnaces by two fluidized bed roasters, fitted with waste heat recovery boilers with a daily output of 150 tons of steam at 30 kg. pressure. As soon as this was done the factory boiler was shut down because all steam requirements were provided by the waste heat recovery boilers.

In 1955 the growing demand for sulphuric acid of Union Chimique Belge called for the installation of new production units; the site chosen was Wondelgem, mainly on account of its being situated near the port of Ghent which gives access to ocean going vessels.

Since a much lower investment was required for a brimstone burning contact plant as compared with pyrites, and as this raw material could be supplied direct and at a reasonable price by vessels leaving the Gulf of Mexico, it was decided to use brimstone as raw



Union Chimique Belge. General view of the two convertor installations at Wondelgem.



material for a new contact plant with a daily capacity of 350 tons (100% H_2SO_4).

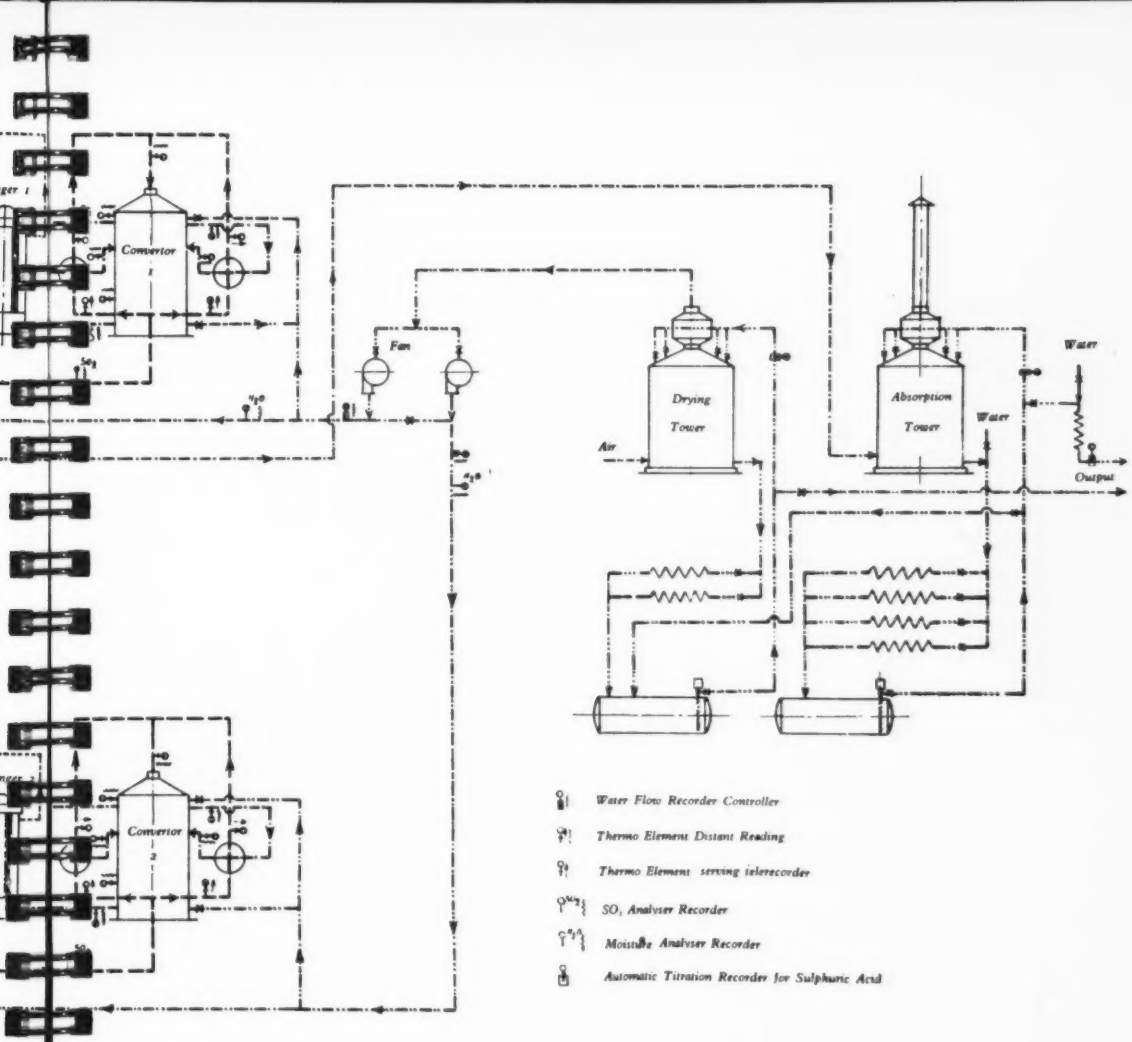
Because all the steam requirements of the factory were already covered by the boilers based on the fluidized bed furnace, it was decided to fit out the new plant with superheated steam boilers feeding a group of turbines.

Description

This plant was built in a new part of the factory and is based on the most modern ideas both in construction materials and general layout of the plant; thus, all the equipment is in the open with the exception of the blowers and the control desk which are in an office underneath the drying and absorption towers.

The daily capacity of 350 tons of 100% acid may be raised to 400 tons by over-running the plant to a certain extent, thus losing a maximum of 1% of the conversion yield. The plant comprises two contact units, that is two groups consisting of a furnace and a converter, but there is only one air-drying tower and one absorption tower for the acid production.

Air for the Furnace: The air is dried by passing through a tower in contact with concentrated sulphuric acid acting as the dehydrator; on leaving this tower the air humidity is less than 0.1 gms. per cm. The drying tower is packed with special rings and has the correct height and diameter to ensure



that the air will be fully dried while no drops of acid will be carried over the air current.

The dry air is sucked in and passed towards each furnace by a blower with a maximum output of 31,000 cu.metres; and in a tubular heat-exchanger it is reheated up to 300°C by the hot converter gases. The air output is adjusted to the sulphur feed so that the SO_2 content of the gases leaving the furnace should be of the order of 11-12% of the volume.

Brimstone Burner: From the storage heap brimstone is moved by a mechanical shovel and loaded into the melter which is fitted with a steam-heated coil. There are two melters, one in service and one in reserve, so that continuity of operation can be maintained while one melter is being cleaned. To neutralise any acidity in the brimstone and combat the corrosive effect of the melted sulphur, lime is added when necessary.

The molten sulphur is pumped by immersion pump to filters consisting of fine meshed stainless steel cloth, then stored in two tanks from which it is pumped on, still by immersion pumps, towards the burners. When bright sulphur is used filtering may be omitted but it is desirable when using dark sulphur containing an excess of impurities.

The melter and storage tanks are constructed below ground level and special attention has been paid to their construction

to prevent seepage of water which would contaminate the sulphur and possibly cause mist formation. The storage tanks are made of concrete and lined with special bricks to protect the concrete from attack by the sulphur; in addition soakaways lower the water table in the surrounding area.

Each burner consists of a brick-lined vertical steel cylinder, 3.1 metres in outside diameter and 8.5 metres high. Air, heated to about 300°C, enters the top of the combustion chamber, together with the molten sulphur, which is pumped through a spray nozzle.

The air input is adjusted to match that of the sulphur and is so controlled that the gas leaving the bottom of the furnace should contain between 11% and 12% of SO_2 by volume; the temperature inside the burner is of the order of 1,100 to 1,200° C.

Boilers: On leaving the furnace the hot gas enters the waste heat boiler which has a heating surface of 310 square metres and is fitted with a super-heater with a surface of 75 square metres. Water pipes are arranged to permit natural circulation.

The gases enter the boiler at about 1,200° C and leave it at about 330° C; stringent precautions prevent an excessive drop of temperature towards the dew point since this would cause rapid corrosion of the equipment. The resultant steam has a pressure of 30.5 kg/square cm. at a temperature of 420° C and each boiler has a capacity of 7.3 tons of steam per hour; they may be overloaded up to 20%. Steam production is practically equal to that of the acid expressed at 100%, that is 350 tons per day under normal operating conditions. The two boilers are completely heat-insulated and lagged, and stand out of doors like most of the plant; they are, however, protected against the weather by a light roof.

The Contact Plant: The gas leaves the boiler, passes through a quartz-filled filter, is re-heated in a double-heat exchanger to the reaction temperature and enters the first stage of the converter in which the SO_2 is converted into SO_3 by passing over four trays of contact mass, of which the second and third trays provide the heat for the double heat exchanger. In addition, heat control in the converter is assured by blowing in dry air after the first and third tray of contact mass.

The converters have an exterior diameter of 5 metres and are built in cast iron with refractory, acid-resistant interior lining. The contact mass of 31.5 cubic metres for each converter, or 63 cubic metres for the whole plant gives a guaranteed conversion yield of over 98%.

On leaving the converter, the gas is cooled in a gas/air exchanger and reaches the lower part of the absorption tower at a temperature between 150 and 180° C, according to the speed at which the plant is being operated.

Absorption: In the absorption tower, which is exactly the same size as the air-drying tower, the SO_3 is completely dissolved in the recycled acid which is maintained at the desired concentration of 98.4%.

Control Room showing flow sheet & recording instruments.

The acid is recycled at a speed of about 300 tons/hour and must be rapidly cooled to counteract the very strong exothermic reaction produced by dissolving the SO_3. An automatically controlled water supply maintains the concentration of the recycled acid at the desired level, the overflow constituting the production acid.

To prevent the entrainment of drops of acid the acid inlet, the gas inlet, and the size of the packing material are kept within narrow limits; in addition, the sprinkler device in the upper part of the tower is designed to avoid spraying the acid onto the packing material.

After passing through a mist precipitator, the tail gas is vented to the atmosphere through a steel chimney and practically no fumes are visible so long as the plant is operated under the proper conditions.

Control Room: All the control and regulating apparatus is centralised at a desk and switches are installed on a flow sheet of the plant. The control room is separated by a glass panel from the engineer's office on one side and the operators on the other, thus grouping in the same place the control instruments and the control post. This logical arrangement of equipment and machinery promotes a high level of operating efficiency and production of the order of 125,000 tons per year of acid may be achieved by a small number of operators. To run the whole plant, including steam generators, each shift consists only of one formeman and two assistants.

Turbo-Generators: The turbo-generator, which is fed by the steam from the waste-heat boilers is situated at some distance from the acid plant. It was considered preferable to instal the turbo-generator near the canal, at the other side of the factory, in order to avoid the high investments and operating costs required to provide large quantities of cooling water at such a long distance.

The set, a single installation, is linked in parallel to the exterior grid at 36,000 volts. If the turbo-generator stops, a desuperheater cuts in, followed by a condenser to recover the condensed steam in view of the high cost of water and of purification. The entire plant consists of:

(a) A condenser turbine: fitted with a single-phase reduction gear to reduce the speed from 5,000 to 1,500 revs./minute. Under full load the turbine develops energy up to the limit of the generator (3,290 KW). Steam is supplied at a pressure of 28 atmospheres and a temperature of 420 C. The turbine running at 5,000 revs./minute, comprises a single-impulse stage for regulation followed by three stages of the reaction type. By the nature of the installation the turbine has to satisfy two overriding conditions: it must consume all the steam produced in the waste heat recovery boilers while maintaining a constant steam pressure: a drop in the pressure would cause a drop in temperature in the boilers, and this might cause corrosion at the cold spots. A control device activated by a servo mechanism automatically regulates the opening of the inlet valve of the pipes to maintain a constant pressure at the entry to the turbine. When operating normally the speed is automatically kept constant as the generator is connected with the grid in parallel. As a safeguard when stopping and starting, or when there are any operating troubles, there is a speed regulator coupled with a pressure regulator. In addition, the

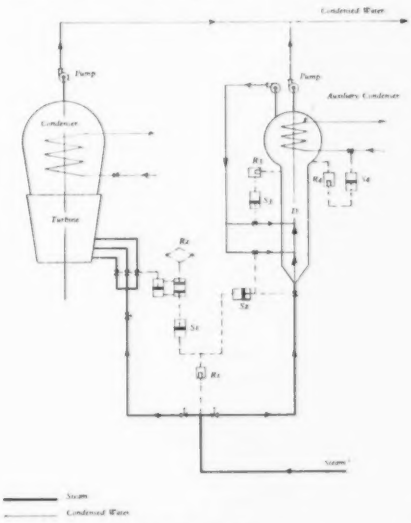


Fig 2. Steam Circuit.

machine is fitted with the usual safety devices to meet all possible contingencies such as: dangerous rise of temperature in the condenser or in the lubricating system, failure of the vacuum, drop of the water feed to the condenser, failure of the electric circuit of the generator or the transformer. Optical and acoustic signals are provided to warn the operator of any disturbance; if he fails to act immediately, the steam is automatically cut off and the generator shut down.

(b) A Condenser equipped with brass cooling tubes, made in two independent parts to allow the tubes to be cleaned without stopping the plant. The plant is designed for a maximum steam intake of 15 tons per hour with cooling water at a temperature of 25 C and a throughput of 1,200 cubic metres per hour. The condensed steam is taken up by the pumps and recycled towards the boilers.

(c) A synchronised three-phase generator of 4,000 KVA capacity at 6,000 volts, speed 1,500 revs./minute. To protect the generator from the possible corrosive effect of

the air from the factory especially as there are a number of chemical plants nearby, the generator air cooling system is in a closed circuit. The cooling air, with a throughput of 280 cubic metres per hour is cooled in a heat exchanger from 65 C to 39 C by circulating water, the temperature of which is raised from 25 up to 35°C. The generator is linked with the public net-work through a 6,000/36,000 Volts transformer. Depending on the steam balance and power requirements of the factory at any time, it is possible either to suplement the output of the generator by drawing power from the net-work or to feed it with the available surplus power.

(d) Whenever the turbine governor closes the steam-admission valve, the steam is automatically by-passed to an expansion and desuperheating device, which expands the 28 atm. steam to 1-1.1 atm. and brings its temperature down from 420°C to 100-110°C. This device can handle a maximum throughput of 15 tons of steam per hour; it operates automatically and permits exact control of the temperature of the outflowing steam, which is condensed and cooled to 85°C before being recycled to the boilers, except for a small fraction which is fed back to the desuperheater.

Conclusion

The thermal energy released during chemical manufacture is recovered in the form of electrical energy in a group of turbo-generators, the output of which supplies the greater part of the energy requirements of this large chemical factory. Heat recovery is nowadays a decisive factor in the economics of sulphuric acid manufacture and this installation at the Wondelgem plant of Union Chimique Belge is an outstanding example of this.

BY-PRODUCT SULPHURIC ACID

Stolberger Zink A.G.

THE COMPANY, one of the leading zinc producers in Western Germany, operates the Nievenheim zinc smelter. This is situated six miles south of Neuss but, although on the Rhine, it receives its ore supplies by rail. Operations are based on a special roasting process whereby part of the ore feed containing about 32% sulphur is pre-calcined in a ten-hearth roaster to produce an intermediate product containing 4½% sulphur which is then pelletised and after being mixed with crude zinc blende, calcines and, if necessary, some other materials, is sintered on a 50 sq. metre belt. The resultant roaster gas is cleansed and converted to sulphuric acid in three vanadium contact converters.

Pre-Roaster

The various grades of zinc concentrates are mixed at the ore dump and carried to a fifteen-floor Büttner turbine drier or to a Büttner drying drum — both oil fired — to reduce the moisture content to 2%-3%. The dried concentrates mixture is carried by a belt conveyor to an ore bunker and thence to the drying hearths of the ten-hearth Chemiebau roasters. The effective roasting surface of each furnace is 270 sq. metres and the throughput about 80 t.p.d. each. About 90% of the lead content of the material is eliminated in roasting. The pre-calcined ore, after passing a coarse mesh grid, is cooled in a drum where it is mixed with moist pellets which it dries. This reciprocal cooling and drying process—the subject of a German patent No. 1013874—produces a mixed material of which the minus 2mm. fraction is passed to the feed end of a dish pelletiser, whilst the oversize (plus 7mm.) is eliminated in a two-tier sieve and after being ground in a roller mill passes to the discharge end of the pelletiser. The intermediate size 2-7mm. is ready to enter the sinter plant. The dish pelletiser consists of two off-set Loesche-dishes on which the fines are pelletised whilst dilute sulphuric acid is added.

By-product Sulphuric Acid Plant

The roaster gases are cleaned in two separate installations working independently, but preliminary dust removal is effected identically in both. Gases pass through a cyclone and balloon conduits. Gases from furnace No. 1 enter a hot gas dust precipitator, pass through a tower and a wash tower equipped with ceramic elements and in which acid is circulating. Finally they enter a wet precipitator. The gases from furnace No. 2 after dust

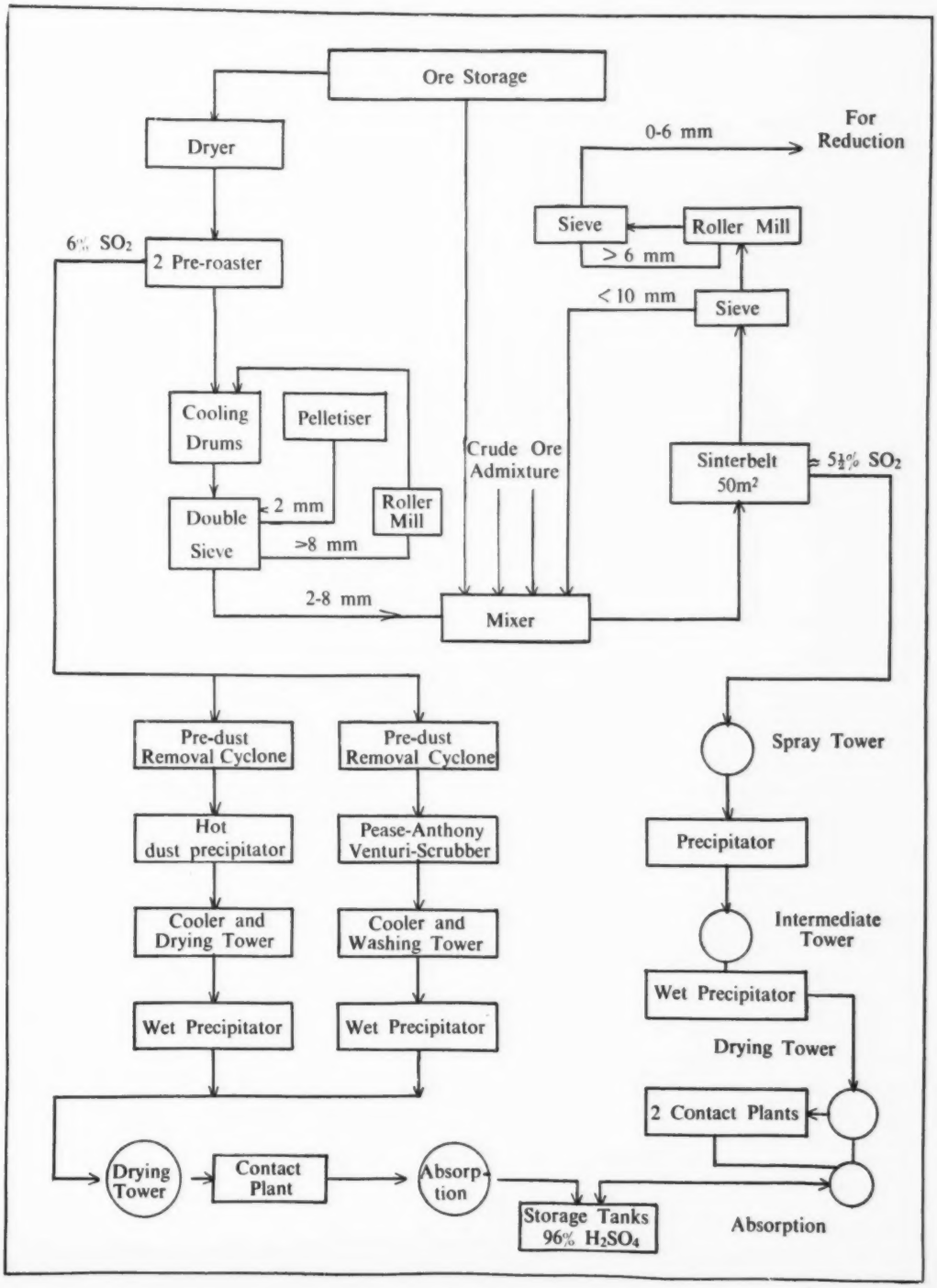

Ore Storage
Dryer
0-6 mm
For Reduction
Sieve
Roller Mill
> 6 mm
6% SO2
2 Pre-roaster
< 10 mm
Sieve
Cooling Drums
Pelletiser
Crude Ore Admixture
Sinterbelt 50m2
5½% SO2
Double Sieve
< 2 mm
>8 mm
Roller Mill
2-8 mm
Mixer
Pre-dust Removal Cyclone
Pre-dust Removal Cyclone
Spray Tower
Hot dust precipitator
Pease-Anthony Venturi-Scrubber
Precipitator
Cooler and Drying Tower
Cooler and Washing Tower
Intermediate Tower
Wet Precipitator
Wet Precipitator
Wet Precipitator
Drying Tower
2 Contact Plants
Drying Tower
Contact Plant
Absorption
Storage Tanks 96% H2SO4
Absorption

Fig. 3

General view of zinc smelter at Nievenheim. Sulphuric acid plant right foreground.

elimination are cleansed in a Pease-Anthony Venturi scrubber fitted to the furnace and are then passed through similar towers to No. 1. The two gas streams join and about three-quarters of the volume of 300 cubic metres/minute is pre-dried, dried and containing 6% SO_2, converted to SO_3 in a 70-ton per day contact installation equipped with a vanadium catalyst. SO_3 gas is absorbed in an absorption tower to monohydrate, which is then diluted and after cooling is transported to storage in the form of 66% Bé acid. The balance of the pre-roaster gas stream is fed to the sinter gas SO_2 gas converter.

Sintering Section and Sulphuric Acid Plant

In the preparation of the sinter feed, pellets from the pelletising plant are pre-mixed on a conveyor with crude blende residue and occasionally other additions, and then mixed in a drum. The feed is carried by a conveyor belt to a storage bin serving the sinter belt. The actual discharge on to the belt is effected by means of a roller and the mixture is ignited by high pressure gas burners. The first six suction boxes carry rich gas which is carried to the gas purification plant. The other six boxes carry a weak gas which circulates. The calcined sinter is coarsely pre-crushed and removed over a vibratory conveyor. A second vibratory conveyor eliminates material under 10mm., the oversize of which is reduced in a jaw crusher. The finished pre-crushed sinter is raised into the storage of a roller mill which feeds into an oscillating sieve separating 5, 6 or 7mm. material. The oversize returns to the storage bunker for coarse sinter and so returns to the grinding circuit, whilst the undersize material is weighed and goes direct to the smelter.

The rich gas is first cooled in a spray tower, cleansed in an electrostatic dust precipitator, and after passing through a tower equipped with acid circulation enters the wet precipitator consisting of a three-stage acid wash tower. The gas—about 310 cubic metres/minute containing 5% SO_2 is mixed with the unconverted pre-roaster gas and is passed through a pre-drier and main drying tower. They are then converted in two Chemiebau contact plants each with 70 tons per day capacity and incorporating a vanadium catalyst. The converted SO_3 gases are absorbed in a tower to monohydrate and after circulating through a cooler are pumped to storage. This consists of four tanks, two of 750 cubic metres and two of 1,000 cubic metres capacity, and is equipped for despatch by road and rail tankers and also by tanker barges as the plant is linked by a 600 metre long gravity feed cast-iron pipe with a discharge point on the River Rhine.

THE KESTNER SPRAY TYPE SULPHUR BURNER

THERE ARE numerous process industries requiring the application of sulphur dioxide either as a gas or in solution form, and in all cases where the consumption is greater than about 40lb./hour SO_2 it is economic to produce the gas from the combustion of sulphur with air. Generally speaking it is only economic to utilise bottled gas where consumption is below this figure.

In generating sulphur dioxide gas it is desirable in most cases to produce the burner gas at the highest possible SO_2 concentration. Theoretically if all the oxygen present in the combustion air is effectively used in combustion of the sulphur, it would be possible to produce a burner gas containing 21% SO_2 by volume. However, the nearer the approach to this theoretical condition, the greater is the danger of unburnt sulphur passing over with the products of combustion. This effect is caused by deficiency of oxygen, and the presence of this sublimed sulphur can cause great difficulties in the gas coolers, and subsequent absorption of reaction equipment, where it will condense and block the passage of the gas. It is, therefore, important in designing sulphur burners to create conditions whereby the highest possible gas concentration can be achieved, without causing the formation of sublimed sulphur.

Another important consideration is size. The longer the contact time required between the sulphur and combustion air to complete the combustion of the sulphur, the larger will be the size of the combustion chamber, with resultant increase in capital cost.

In addition, it is also desirable that the unit should have as much flexibility as possible, so that it may be operated when necessary at lower throughput levels than the designed maximum.

In all operations involving the reaction or combustion of a liquid with a gas, such as the combustion of molten sulphur in air, the rate at which the reaction may be driven to completion is directly related to the following factors :—

(1) Surface area between the gas and liquid—the greater the area of contact the greater will be the rate of combustion.

(2) Turbulence in the gas phase—the greater the turbulence imparted to the combustion air, the greater will be the combustion rate, since the resistance of the gas film on the surface of the molten sulphur will be reduced.

In conventional burners of the hearth, cascade, and rotary types, the molten sulphur is caused to flow over the hearths, or in the case of the rotary burner, over the walls of a rotating cylinder, while the combustion air passes over its surface. Using this method where combustion takes place over the surface of a pool or film of molten sulphur, the surface area is limited while no very great degree of turbulence is imparted to the combustion air.

These types of sulphur burner are normally operated to give a sulphur dioxide concentration of 10-14% v/v. In the spray type sulphur burner, however, a great increase in surface area is achieved by spraying the molten sulphur into the combustion chamber through an atomising nozzle. The molten sulphur is then exposed to the combustion air in the form of a fine mist. The rate of combustion is considerably increased, and a gas concentration of up to 18% v/v may be obtained without causing the formation of sublimed sulphur. These features apply to all types of spray burners in which, however, special consideration is rarely given to imparting turbulence to the combustion air. As this factor considerably influences the combustion rate, plant size and capital cost are consequently also affected. In addition, some types of spray burners rely on pressure jet atomisers, which require changing if an appreciable reduction in throughput is required so that flexibility is limited.

In the Kestner spray type sulphur burner the generic advantages of the spray type burner are employed, but in addition, the combustion air is injected into the combustion chamber at high velocity resulting in an exceptionally high degree of turbulence and a very great increase in combustion rate. This reflects on

the size and capital cost of the burner which occupies only a fraction of the space required for conventional units. The atomiser is also designed to give flexibilty of operation since the sulphur is atomised by a jet of hot air, and does not operate on the pressure jet principle alone.

As shown in figure 5, molten sulphur is circulated through the melter either by an immersed or steam jacketted sulphur pump, the required quantity of sulphur being bled through the control valve to the sulphur atomiser. All piping and valves are steam jacketted. The molten sulphur is injected into the combustion chamber through the central nozzle of the atomiser in the form of a hollow, thin-walled cone. At the same time a small flow of primary atomising air, provided by the primary air compressor, is heated to about 130°C and fed to the atomiser. This flow of primary air is introduced into the combustion chamber at high velocity through an annular orifice which surrounds the central sulphur jet and impinges on the walls of the cone of molten sulphur, breaking up the sulphur into very fine droplets.

The combustion chamber itself is constructed of two conical sections bolted together, there being a small parallel section between the two cones. The walls of the chamber are constructed of high temperature refractory and the conical sections are provided with a number of ceramic nozzles, through which the secondary or combustion air is introduced. The secondary air is provided by the compressor shown and is injected into the chamber at high velocity through the ceramic ports. The air and sulphur are contacted under highly turbulent conditions, ignition is provided by means of a gas pilot flame, and sulphur dioxide gas is generated at any concentration up to 18% v/v, depending on the relative rates of flow of sulphur, and secondary combustion air. The burner gas leaves the combustion chamber through a refractory lined water-cooled tube where any traces of unburnt sulphur are finally burned off and the gases pass through the coolers to process.

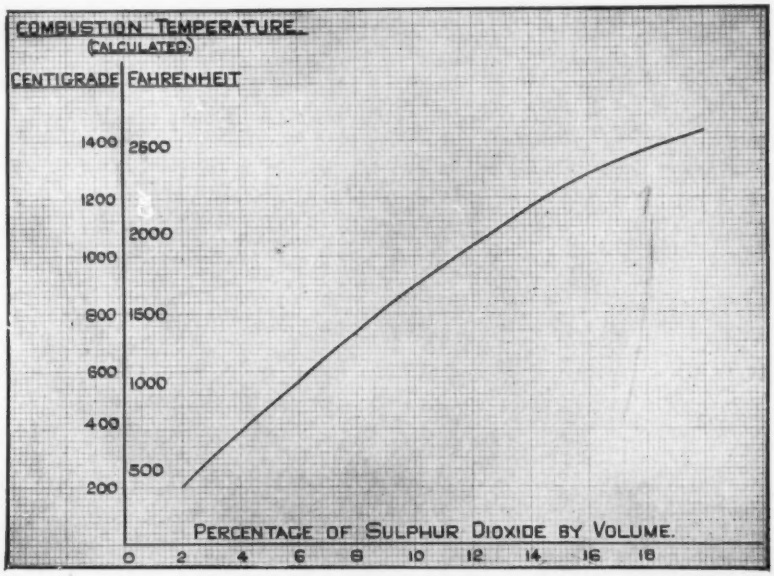


Fig. 4

Flexibility of throughput is assured by the atomiser design which relies mainly on the flow of primary air for effective atomisation. The flow of sulphur to the atomiser may be regulated by the control valve on the sulphur feed line, while concentration of the gas is governed by the flow of secondary air.

Instrumentation can be kept simple and all that is essentially needed to obtain an indication of operating conditions is an orifice meter to measure the secondary air flow and a

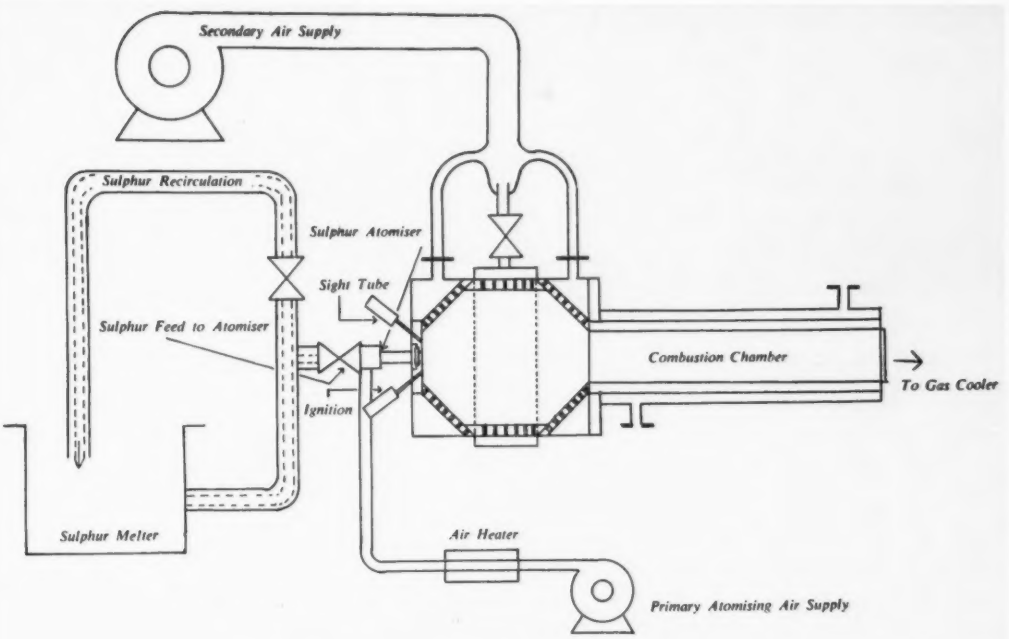


Fig. 5. Flow diagram of Kestner Spray Type Sulphur Burner.

thermometer to register the temperature in the furnace. The furnace temperature is directly related to gas concentration so that by establishing the secondary air flow at a rate corresponding to the desired sulphur throughput it is only necessary to adjust the sulphur feed to maintain the furnace temperature which corresponds with the gas concentration required.

The type of burner described is manufactured in various sizes, capable of handling from 1cwt. to 2 tons per hour of sulphur. The 1cwt. per hour size burner does not exceed 22" diameter by an overall length of 8 to 10ft., while a 2-ton per hour burner might measure approximately 4ft. diameter, depending on the required operating conditions.

The application of spray type sulphur burners covers many industries, but without doubt the largest of these is the manufacture of sulphuric acid. Here, although a highly concentrated gas is not required, the flexibility and low space requirements of the spray type burner when handling sulphur throughput rates of the order of 2 tons/hour offer considerable advantages. Virtually all sulphur burning sulphuric acid plants now installed incorporate spray type burners although not necessarily incorporating the principle of gas turbulence.

In the manufacture of sulphite, bisulphite, and sulphur dioxide solutions, for the paper and starch industries, for example, the burner gas must be absorbed in packed towers by alkaline solutions, or by water, and in this type of process the size of the absorbers are directly related to the concentration of the burner gas. By using the spray type burner delivering the SO_2 gas at concentrations of 18% v/v it is possible to reduce the size of the absorption towers to a considerable extent, thereby reducing the overall capital cost of the plant. It is also possible to obtain more concentrated liquor solutions from the absorbers than with other types of burner.

The flexibility and instantaneous control which may be achieved with the Kestner sulphur burner and burners of similar type and design, coupled with the high SO_2 concentration of the burner gas, can be said to offer considerable operational and economic advantages.

DESULPHURIZATION OF COKE OVEN GAS

The Still Process

General

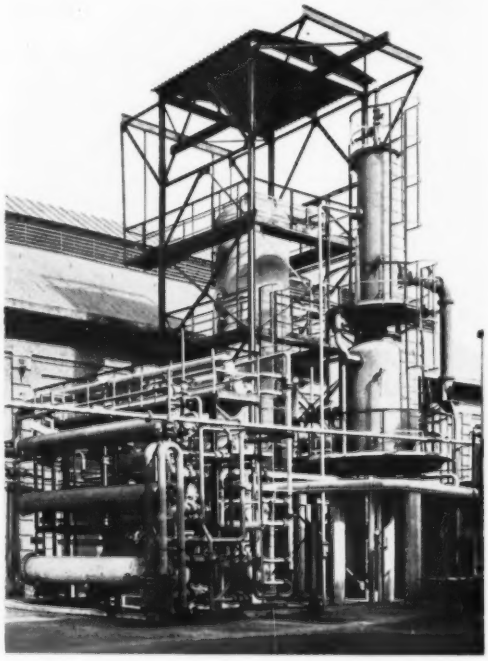
THE EARLIEST attempts to effect efficient desulphurisation of coke oven gas, by recirculating ammonia produced at the same plant, can be traced back to the latter half of the 19th century. In contrast with the requirements of town gas manufacture there was not the same need for sulphur removal at coke-ovens and due to unfavourable economics, this method of gas pre-purification did not receive much support.

During the past 15-20 years the problems involved have again received more active consideration. This is partly due to the need at coke oven plants to increase utilisation of coal by-products and the growing volume of gas purchased by town gas works from coke-ovens. In this connection many laboratory and large-scale tests have been carried out and a number of processes put into operation. Resulting from this experience, equilibrium processes using ammonia as the scrubbing medium are particularly favoured. Owing to the difficult problem of corrosion, the search for suitable materials of construction involved much work, and numerous tests were carried out to ascertain the mutual reaction of ammonia, hydrogen sulphide and carbon dioxide in the absorption process and in the regeneration of the scrubbing medium. In addition, difficulties were encountered in the processing of ammonia to ammonium sulphate.

Firma Carl Still of Recklinghausen and *International-Carl Still Ltd. of London* have studied the close association between ammonia removal and the recovery of hydrogen sulphide from coke oven gas, and have made important contributions to the developments in this field. During the last four years they have constructed a number of plants, based on their process, and these are operating to their clients' satisfaction. In the account which follows a short description of the process is given, together with operation data from these installations which have been designed with the object of obtaining efficient preliminary desulphurisation of gas by ammonia liquor in co-ordination with existing liquor distillation and ammonia recovery plant.

Process Description

Different methods of H_2S scrubbing have been developed for the various processes of ammonia recovery. For this reason both the indirect and direct processes have to be considered. With the indirect method the ammonia scrubbed from the crude gas is processed either to ammonium sulphate or to concentrated



General view of a "Still" installation for the wet desulphurisation of coke-oven gas.

ammonia liquor. For the semi-direct process two different methods have been developed for low-pressure and high-pressure scrubbing respectively. The process for H_2S scrubbing in conjunction with indirect ammonia recovery (as ammonium sulphate) is described here in detail and is illustrated in figure 6.

The crude gas is sufficiently cooled before it enters at the bottom of the combined

ammonia/hydrogen sulphide scrubber. A special design ensures that in the bottom part of the scrubber the bulk of the hydrogen sulphide is removed from the gas, while in the upper part the ammonia is extracted. Weak ammonia liquor enters the bottom section of the scrubber, whilst part of the available cooled virgin liquor or condensate is introduced into the scrubber at a higher level and softened fresh water enters at the top for the final scrubbing of ammonia.

direct and indirect cooling, are delivered by means of a blower to a combustion chamber where they can be processed to sulphuric acid, or, alternatively, elemental sulphur.

The liquor from the decarbonator, containing ammonia, is passed to a second distillation column (ammonia still). The gases leaving at the top of the still are condensed through heat exchange with the enriched ammonia liquor from the scrubber and absorbed completely in the surplus condensate and cooled

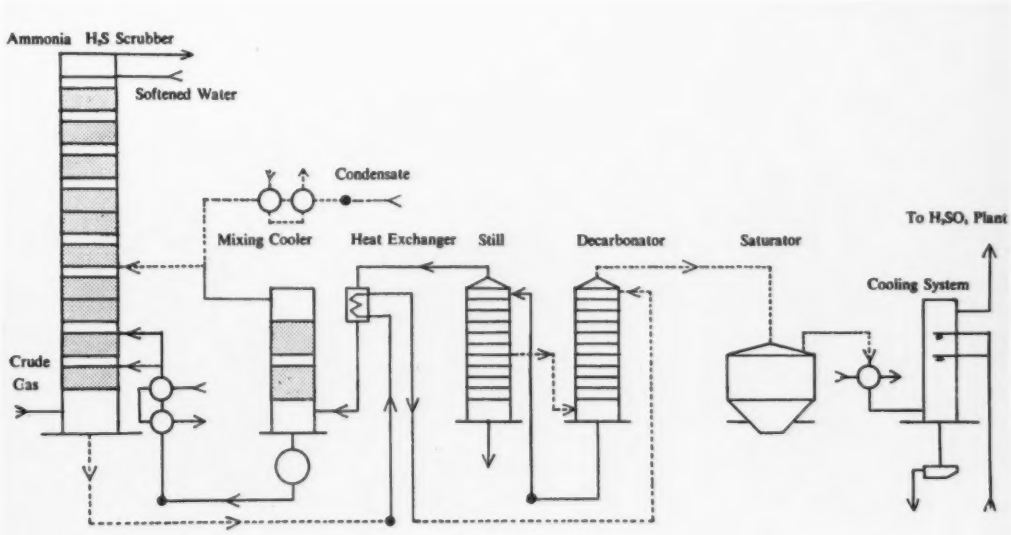


Fig. 6. Ammonium sulphate recovery by indirect process.

Hydrogen sulphide enriched ammonia liquor from the combined NH_3/H_2S scrubber is preheated in a heat exchanger and then passed to the distillation column (decarbonator). The hydrogen sulphide, carbon dioxide, hydrocyanic acid and ammonia present in the washing solution are liberated by steam and are passed from the top of the column to the saturator, where the ammonia is absorbed in sulphuric acid and crystalline ammonium sulphate is formed. Vapours leaving the saturator consisting of hydrogen sulphide, carbon dioxide, hydrocyanic acid and air, which is used to agitate the saturator charge after

in the final mixing-cooler. Weak ammonia liquor produced in this way is cooled and returned to the scrubber.

In order to obtain maximum removal of impurities from the gas it has been found that it is desirable to maintain the ammonia liquor introduced in the scrubber at a low temperature. In this manner the high temperature resulting from the heat of solution in the upper part of the scrubber can be controlled. At one plant, where the throughput of coke oven gas (density 0.026 lb. ft.^{3}) is 20.5 million cubic feet per day (n.t.p.), the average operating temperature of the scrubber is 20°C, and the pressure loss does not exceed eight inches W.G.

If it is not desired to produce ammonium sulphate the plant can be modified so that part of the ammonium is removed as concentrated liquor, illustrated in figure 7. Cold condensate and weak ammoniacal liquor would be introduced into the decarbonator and the ammonia gases would be taken off from the top of the still instead of from the decarbonator. Additional coolers would be introduced for condensing these gases.

dry purification process. Fresh and cooling water needs are moderate.

The steam for the process is first introduced into the distillation column (ammonia still) where it is used to remove the free ammonia from the effluent to the extent of about 3.5 grains/gallon. Steam for the decarbonator is taken from the middle section of the ammonia still. Total steam consumption is very low and may be only about 12lb./1,000 cubic feet of gas

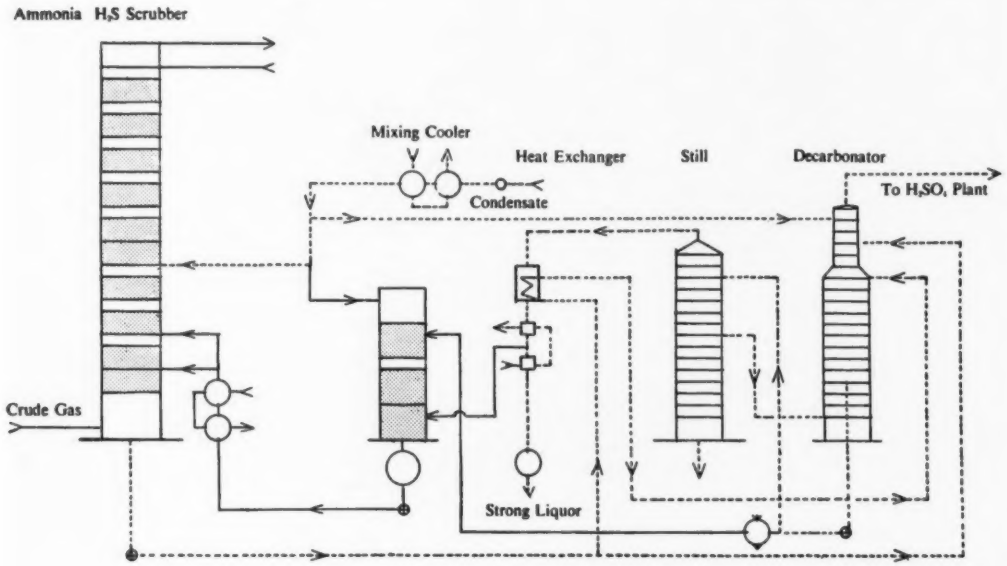


Fig. 7. Strong ammonia liquor recovery by indirect process.

Operation data

Results recently obtained at plants using the Still process show that a high scrubbing efficiency can be obtained even with a low content of hydrogen sulphide in the crude gas; thus with crude gas containing 250 grains H_2S per 100 cubic feet a scrubbing efficiency of over 80% was obtained. The ammonia content in the gas was reduced from 200 grains per 100 cubic feet to 0.08 grains per 100 cubic feet.

Electric power and condensate requirements for the hydrogen sulphide removal are low when compared with the value of sulphur or sulphuric acid recovered and compare favourably with costs normally charged to the at S.T.P. when the hydrogen sulphide content is 450 grains per 100 cubic feet and the plant is operating at 80% recovery.

Conclusion

Operation of the "Still" process on a commercial scale has proved that the close combination of ammonia recovery with the pre-desulphurisation of coke oven gas can be an economic proposition, particularly when the throughput of gas exceeds 10 million cubic feet a day. In addition to important by-products there are the advantages of sulphur-free gas which not only make the gas itself a valuable product, but also reduce problems of air pollution with their attendant costs.

Sulphur Recovery from Hydrogen Sulphide

New type small scale plant

UNTIL RECENTLY the recovery of sulphur from small volumes of hydrogen sulphide discharged to the atmosphere by way of exhaust stack gases has, with few exceptions, proved uneconomic and in most instances to ensure profitable operation at least 20 tons of brimstone had to be produced.

Pan American Petroleum Corporation of Tulsa, Oklahoma, has introduced process equipment modifications to the established Claus process which now permit sulphur recovery on as small a scale as three tons per day. Subsequently Tears Engineers Corporation of Dallas, Texas, working under licence to Pan American Petroleum Corporation further modified the design in making the recovery plant more compact and in placing it on skids, thereby giving the equipment greater mobility and flexibility of operation.

The key item of equipment is a multi-purpose five-pass marine type boiler. Additional equipment includes a two-part convertor containing bauxite catalyst, a combined sulphur separator and storage tank, air blower, pipe links and controls. In operation feed gas and air enter the combustion tube of the boiler through a special burner nozzle. This nozzle metres one-third of the H_2S feed direct into a fresh air stream burning it to sulphur dioxide. The remaining acid gas flows into the tube along a different route. The second pass is a cooling stage. The exit gas from this stage containing some sulphur vapour from non-catalytic reactions in the first two stages flows through the third pass, a partial condenser, and then into the tank for separation of liquid sulphur. At this stage about 40% of the recoverable sulphur has been obtained. Gas emerging from the storage tank mixes with the hot exit gas from the second pass and reacts over the catalyst in the first compartment of the convertor. The resultant sulphur con-

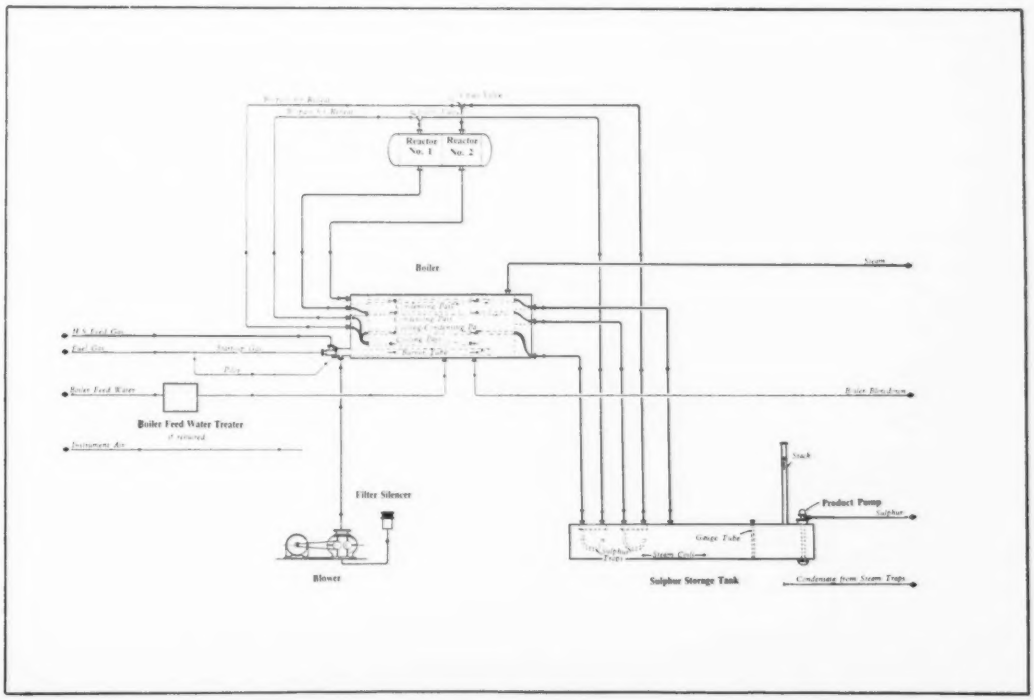
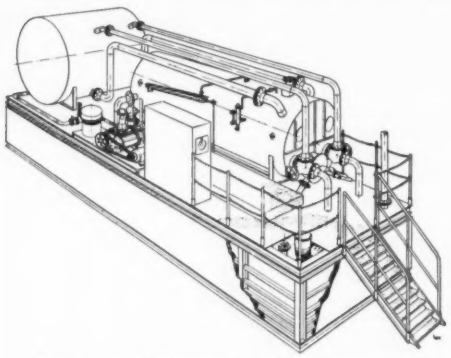


Fig. 8

denses in the fourth boiler pass and runs to storage. This conversion cycle is repeated again in the second convertor stage and the fifth boiler pass. Any acid gas remaining, leaves through the mist precipitator and exit stack. Process heat is recovered in the form of saturated steam 20-40 p.s.i.g. at a rate of 250 lbs. per hour, for each ton of daily sulphur production. To minimise the power needs of the process air blower the units operate at 3 to 4 p.s.i.g.

The sulphur recovery plants are designed to be as nearly automatic as possible. The heart of the control system is a flow instrument which controls the ratio of the volume of air



Tears type skid-mounted sulphur recovery unit.

to feed gas. It operates from a flow meter in the feed gas stream and as its rate changes the air rate follows accordingly. Dependent upon local conditions the operator makes periodic analyses of the stack gas in order to determine the gas composition, which in turn determines the air to feed gas ratio. The boiler feed water controls are also automatic. The main duties of the operator, therefore, are the maintenance of correct level of sulphur in the storage tank and its removal to trucks or secondary storage as the built-in storage is designed for only three or four days output.

The Tears type plant enjoys significant cost advantage over conventionally built plants. The principal reason for the lower cost of the plant is that the condensers handling the product gas from the converters are located in the top portion of the boiler or furnace. Thus, the furnace in the Tears design serves a dual function in that one-third of the H_2S is oxidized to SO_2 in the combustion chamber of the boiler while the upper portion of the boiler serves to house the product gas condensers. In the conventionally designed plant there is ordinarily a separate condenser to handle the product gas from each convertor. This arrangement of course, requires associated piping which not only tends to complicate operations but requires additional material and installation costs.

The single-skid mounted units can handle 3 to 12 long tons daily of sulphur. The largest unit is about 30 feet long and 10 feet wide and the operating platform is about four to five feet from the ground. For units requiring an output of 12 to 50 tons, each individual component is separately skid mounted. The maximum capacity considered reasonable for this particular design is about 50 long tons per day. Additional capacity could be handled by the use of a second boiler and an extra convertor or by the use of oversized convertors to handle gas from both boilers. The costs of the recovery units vary accordingly to application; factors that would dictate a change in the cost of these plants are boiler feed water treating requirements, steam condensing equipment in instances where there is no use for the steam or the presence of inert gases (such as CO_2 or nitrogen) or hydrocarbons in the feed gas.

The Pan American Petroleum Corporation have two plants in operation; one with a daily capacity of 12 to 15 long tons has been in use for two years, and the other with a daily capacity of 25 long tons for several months. In neither case have any operating difficulties been experienced. A third plant with a daily capacity of 10 to 12 long tons is now under construction.

The outstanding feature of the Tears type sulphur recovery plants is their extreme mobility and suitability for employment under a wide variety of conditions. Of these the fight against air pollution at works which discharge waste hydrogen sulphide as a result of their normal manufacturing operation is a notable example especially as in most cases these small arisings of H_2S have in the past defied economic recovery except under very favourable operating conditions.

SULPHUR BURNING IN A FLUIDISED BED

THE COMPLETE patent specification for a new method and apparatus for burning sulphur, applied for by the Commonwealth Fertilizers & Chemicals Limited, was accepted on the 10th November 1957. It relates to the improved combustion of dark bituminous sulphur to sulphur dioxide for sulphuric acid manufacture and employs the principle of a fluidised bed.

Description of Process

The method of burning entails the sulphur being directed onto a bed of inert particulate material within a combustion chamber and passing air or other oxygen-containing gas upward through the bed at a velocity such as to maintain it in a fluidised condition. Moreover, the quantity of air or oxygen containing gas supplied to the bed is sufficient to support the combustion of a small proportion only of the sulphur and it also supplies the necessary additional air or oxygen-containing gas to the combustion space above the fluidised bed. The volume of the air or oxygen-containing gas is so controlled that it supports the combustion of an adequate proportion of the sulphur to generate sufficient heat to ensure that bituminous complexes present in the sulphur bearing material are vapourised or decomposed whilst at the same time an excessively high temperature at the bed surface is avoided. The proportion of the sulphur burnt in the fluidised bed, which is situated in the reduced lower end of the chamber, is about 10% of the combustible sulphur in the material.

The sulphur burner shown in the drawings comprises a vertical firebrick cylinder (10) equipped with a domed firebrick roof (11) and with a coaxial downwardly convergent or trumpet-shaped bottom (12) of refractory material. The reduced lower end of this trumpet-shaped bottom is equal in diameter to and communicates freely with the upper end of a cylindrical fluidised bed chamber (13) which has a refractory lining and which is of substantially smaller diameter than the combustion chamber. For example the internal diameters of the cylinder (10) and chamber (13) may be 18 feet and 4 feet respectively.

The chamber (13) contains a bed (14) of sand or other suitable inert material and an inclined feed pipe (15) is provided for supplying coarsely ground sulphur onto the surface thereof. A number of nozzles (16) are mounted vertically at the base of the chamber (13) and air is admitted to the bed through these nozzles

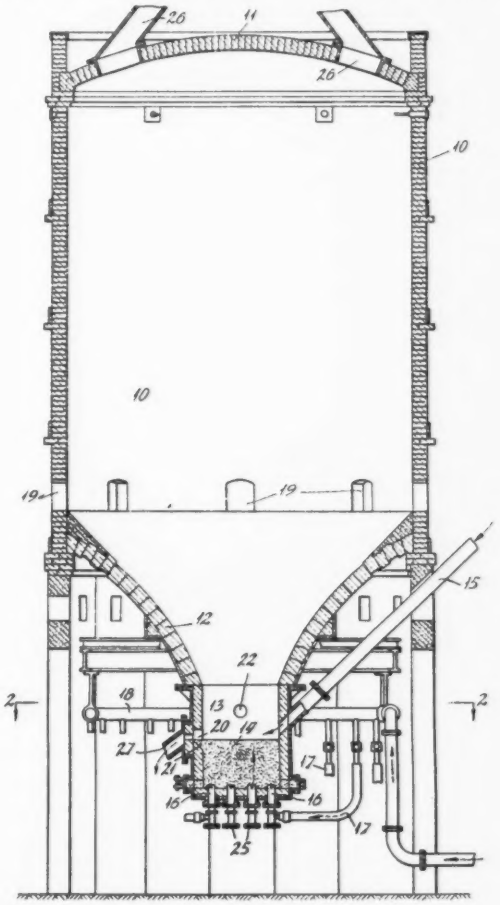


Fig. 9. Vertical section of sulphur burner.

at a controlled rate. Conveniently 12 air blast nozzles are employed and the velocity of the air blast is such as to maintain the bed in a fluidised condition. The air supplied through the nozzles is preferably such that only about 10% of the sulphur feed can be burnt in the

bed. To balance the resistance of the bed only a small portion of the total combustion air need therefore be compressed.

Air is supplied to each nozzle (16) through a corresponding flexible hose (17) from a supply pipe (18) which is arranged concentrically around the chamber (13) as shown in figures 9 and 10.

The bulk, preferably some 90% to 95%, of the air required for combustion of the sulphur is admitted in any convenient manner to a lower portion of the main chamber and in the illustrated construction this air is supplied through some or all of a number of cleaning and inspection openings (19) which when the apparatus is in use are bricked up except for the provision of some air inlet openings. Alternatively the main combustion

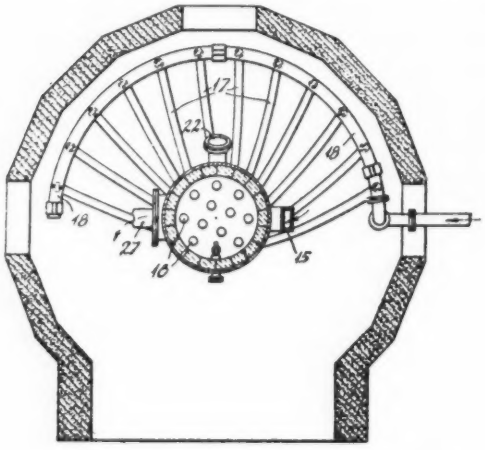


Fig. 10. Cross-section of sulphur burner through line 2-2 of Fig. 9.

air could be supplied through ports formed in an upper portion of the trumpet-shaped bottom (12). The mixture of SO_2 and unburnt air is withdrawn through passages (26) in the roof (11) and are directed to an acid making or paper bleaching plant or the like.

The output may be increased by providing cooling facilities in the combustion chamber, for example by means of water tubes—for this purpose preferably double walled cooling tubes—installed from the top (11) of the combustion chamber. It has, however, been established that a satisfactory output can be obtained without providing the combustion chamber with cooling means.

Temperature control of the fluidised bed is achieved by varying the rate of air admission to suit the feed rate of sulphur. Thus, when burning bituminous sulphur for example the bed surface may be raised to a sufficiently high temperature to effect the decomposition of the carbon sulphur complexes which are produced, whereas previously these complexes have generally been troublesome. If the air blast rate has to be raised, substantially coarser sand or other inert material has to be used, since otherwise the fine sand would be blown from the bed.

A discharge opening (20), the lower edge of which forms an overflow weir (21), is formed in the wall of the chamber (13) diametrically opposite the sulphur feed pipe, the weir being approximately level with the surface of the bed; an inclined discharge pipe (27) directs the overflow material into a suitable receptacle or chute. A portion of the sand forming the bed may be carried over the weir together with the impurities fed in with the sulphur, but the sand so discharged may be sieved out from the impurities and used again. Under such conditions it is necessary to add make-up sand to the bed at suitable intervals. Fine sand may also be blown upward into the combustion chamber but as it tends to settle on the conical bottom it will generally fall back on the bed.

Additional air may be admitted through the sulphur feed pipe (15), the discharge pipe and the illustrated viewing tube (22) in order to prevent sulphur vapour from condensing in the cool spaces which these provide.

The air admission nozzles (16) (figure 11) comprise a conical or cylindrical tube (16a) which is secured at its lower end to a suitable support (23) and is arranged to project upward through a corresponding aperture at the base of the chamber. The tube (16a) is closed at its upper end and has around its periphery a number of small holes (16c) which communicate with the interior of the tube and which are located just above the floor of the chamber.

The open lower end of each nozzle tube (16a) is secured to a hollow base (24) to which the respective air supply hoses (17) are connected. A removable closure plate (25) is

fixed to the lower end of each nozzle base (24) to permit inspection and cleaning.

An advantage of this nozzle construction is that the air hose (17) may be removed from a nozzle or if it is desired to clean or inspect a nozzle this may be done while the burner is

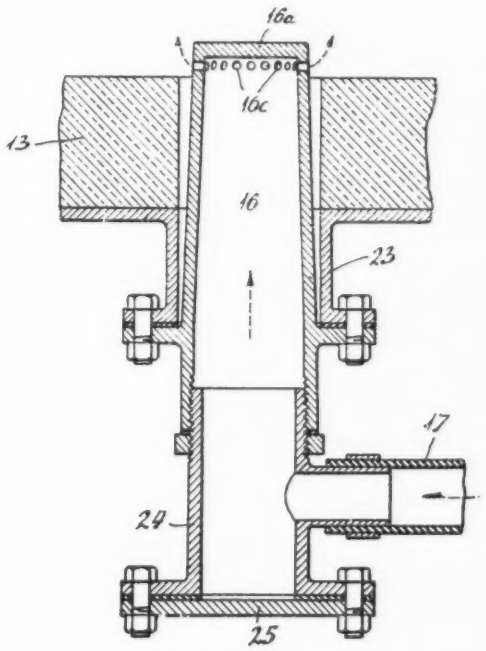


Fig. 11. Vertical section of air nozzle.

working, without adverse results. Under such conditions the small discharge holes (16c) in the upper end of the nozzle tend to choke, thus preventing back-flow of material. These holes (16c) may advantageously be about a quarter of an inch in diameter.

Raw Materials

The inert material employed in the fluidised bed is preferably sand of a suitable degree of fineness, but other inert particulate material may be employed.

Operations

The burner was installed at a new factory at Albany, in Western Australia, in 1954, and has been operated almost continuously for the past four years at various throughput levels of up to 40 tons of dark sulphur per day. This is by no means the capacity, which is rated at 25% greater, but is the maximum demand made upon the plant to date.

One man per shift is all that is required to operate the acid plant including the burner, which is self cleaning. There have been no significant modifications, little trouble and the maintenance cost is well within the accepted range for such equipments.

In the burner used, which was as shown in the drawings, the fluidised bed chamber (13) had a diameter of four feet and a depth of five feet three inches, and the combustion chamber (10) had a diameter at its widest part of 18 feet and a depth of approximately 32 feet from the roof (11) to the top of the fluidised bed.

Gas was drawn from the burner by the plant suction at the rate of 3,400 cubic feet (n.t.p.) per minute, while the air at the rate of 240 cubic feet (n.t.p.) per minute was supplied to the bed (13) through the nozzles (16) at a pressure of about 20 inches water gauge, the remaining 3,160 cubic feet of air per minute being drawn in through the openings (19).

When burning sulphur at a rate of 28½ tons per 24 hours the temperature in the upper part of the burner was about 1,000° C and the discharged gases contained approximately 13% SO_2. The burner was very flexible in operation as the capacity range without providing heat removal elements was from 18 to 30 tons of sulphur per 24 hours, while still providing conditions favourable to the operation of an acid plant. The size range of the sand supplied to the bed was for one test:—

Tyler Mesh ...	−20	−30	−40	−60	−80	−100
% through ...	100	83	62	35	18	2

and the size range of the sand overflowing the weir was:—

Tyler Mesh	−20	−30	−40	−60	−80	−100
% through	99.5	99.5	85.0	11.0	0.75	0.25

An important advantage of the burner is that when the feed is turned off, the bed is almost immediately free of sulphur vapour. This means that rapid control is possible and if the acid plant is shut down quickly there is substantially no reservoir of molten sulphur to continue burning.

Instead of air, other oxygen-containing gases may be supplied such as sinter or smelter gases containing dilute SO_2.

Brimstone Burning Contact Acid Plant

Moritz TAB System

DEVELOPED by Entreprise R. et J. Moritz, of Chatou, Nr. Paris, the French chemical plant manufacturers, for the use of producers of small tonnages of sulphuric acid, the design of this plant is covered by international patent. Its capacity ranges from 5 to 30 tons per day of 98% H_2SO_4, and to date one plant has been erected with a capacity of 12 tons H_2SO_4 producing directly 54/56° Bé. acid (67/69% H_2SO_4). If required plants may also produce monohydrate or oleum.

The entire plant is housed in one building which is sub-divided into two parts with a control laboratory in the middle. The storage section situated in one half may—except for being roofed over—be left in the open air; the contact section which is housed in the other half and may be enclosed on three sides, but if so there must be large air vents under the eaves.

The total floor space required for a 30 ton per day of 98% H_2SO_4 plant is 62′ x 43′ x 17′ high, exclusive of acid and sulphur storage.

Technical Description

The sulphur is loaded in predetermined quantities into the sulphur bunker which is just above the sulphur burner. The sulphur burner is a horizontal steel tank of welded construction lined with firebricks and divided horizontally into sections; the solid brimstone is fed into the top of the burner by means of a screw conveyor feed placed just beneath the bunker. The brimstone is melted by dried combustion air, which has been heated by passing through the lower part of the burner. The molten sulphur flows over the burner sections and the resultant sulphurous gases pass into the combustion chamber. This consists of a vertical steel vessel, firebrick lined, where the quick turbulence given to the gases completes the combustion and a burner gas of the desired composition (11.5%-13% of SO_2) is produced. At the top, on the side of the sulphur burner is an oil burner, fed by preheated oil through a pump, which heats the sulphur burner at the commencement of the operation.

The burner gas is cooled by a waste heat boiler and the temperature of this gas circuit can be regulated by a by-pass valve.

The waste heat recovery boiler of fire tube construction according to the Babcock and Wilcox system, comprises inlet and outlet gas boxes lined with firebricks. The boiler operates at a pressure of 367 p.s.i.g. and as the Moritz burner does not require steam to melt the sulphur, all the steam produced, 24 cwts. an hour, is available for use outside the plant. The boiler is fed by an electrical pump and steam driven pump, which should both receive demineralized water from the power station preheated to 80/100° C. The electrical pump serves at starting-up and as a standby.

The convertor is a Moritz three-pass horizontal type, and is provided with a hot gas filter at one end. Grids are fitted inside the convertor to carry the catalyst which consists of I.C.B. Vanadium Mass laid on graded quartz. Cold dried dilution air enters between the passes in order to obtain maximum transformation efficiency and the SO_2 strength at the convertor is reduced to 7%. Conversion efficiency, it is stated, may reach 98%.

The SO_3 leaving the convertor is delivered to a Moritz turbo-absorber, which consists of a heavy steel vessel, cylindrical in shape, lined with acid resisting materials and provided with a Moritz turbo-absorber model TAB within which intimate contact is ensured between liquid and gas. The bulk of cold absorption acid is divided into fine streams and put in contact with the SO_3 gas to produce sulphuric acid. The moving parts are constructed of a special allow whereas the static parts are made of a natural silica ; these materials are said to have given satisfactory results.

A circuit of pipes, circulation tank, pump and coolers ensures a methodical movement of the acid, whilst the grade is controlled and adjusted in the circulation tank by addition of water through a rotameter. The circulation pump is of the centrifugal type, submerged in the acid in the vessel and the cooler consists of a nest of cast-iron pipes, arranged in parallel banks and sprayed outside with cooling water. The acid produced flows by gravity into the storage tanks passing through a distribution

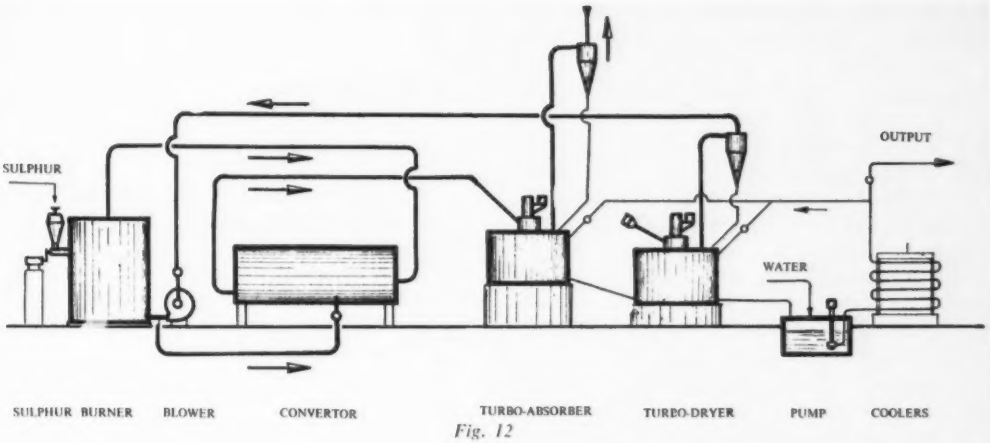


Fig. 12

box with four outlets, one for each storage tank. These tanks are connected to a pumping vessel in which an acid pump is immersed and from this pump the acid stored may be removed for use or onward transportation. After having gone through a turbo-dryer of similar design to the turbo-absorber, air from which dust and moisture has been removed is circulated through the entire plant by a blower.

Operation

The operation of this type of plant is simple and from the entry of brimstone to the final yield of sulphuric acid, labour requirements are limited to one man for an eight hour shift.

The conversion efficiency of the plant is 96%, and the power requirements ratio is 25/37 Kw. for each ton of 67% H_2SO_4

The Vanadium Mass catalyst known as I.C.B., is that made by the Soc. Industrie Chimiche Dr. Baslini of Italy, for which Moritz Chemical Works have exclusive selling rights. In this connection it is of interest that this type of catalyst-installed in a contact plant at Nitrogen Fertilizers Limited's plant in England in 1939 is stated not to have required replacement until 1957.

When burning sulphur of 99.95% purity the gas filter has only to be cleaned approximately every 6 to 10 months.

Conclusion

In view of the low capital cost of the plant (including catalyst) of about £22,000 for a 12 ton per day (100% H_2SO_4) plant, and low operating costs, it appears to be of special interest to the small sulphuric acid producer or chemical works and lesser fertilizer factories.

FERROUS SULPHATE MONOHYDRATE

A New Source of By-product Sulphur

THERE ARE few processing industries which have not to contend with an effluent problem, and who aim to solve it by turning the effluent into a useful by-product. Among these industries the producers of titanium have been particularly confronted with the problems of disposal of copperas or ferrous sulphate. Several processes have been or are being employed to obtain ferrous sulphate monohydrate ($FeSO_4.H_2O$) from copperas ($FeSO_4.7H_2O$), but many difficulties have been experienced. Copperas yields the monohydrate as a result of simple evaporation but during the process the copperas tends to melt in its own water of crystallization with the production of a glassy scale on the heat transfer surfaces, thereby restricting further dehydration. Even in the case of rotary driers the crystals tend to set in lumps which still contain a high proportion of water. Although preparation of the monohydrate has been achieved by spray drying, resulting in a satisfactory product and avoiding the above difficulties, the quantity of water required to make

a satisfactory feed solution presents its own problems. The proportion of water to be evaporated per mole of $FeSO_4$ is more than 15.6 with consequential heat requirements.

In a recently accepted British Patent No. 800,410, British Titan Products Co. Ltd., one of the largest United Kingdom producers of sulphuric acid, describe a process for producing ferrous sulphate monohydrate from copperas which, it is claimed, overcomes the above problems giving efficient and economic results. It involves preparing a slurry suitable for spray drying whilst avoiding high temperatures in dehydration yet not requiring uneconomic amounts of heat in the spray drier due to the low $FeSO_4 : H_2O$ ratio of the slurry. The end product obtained is free flowing as long as total moisture present does not exceed a ratio of $FeSO_4 : 2.5H_2O$, although it is better if the moisture content is no higher than a ratio of $FeSO_4 : 2H_2O$. Two methods are described.

The process which is preferred is basically in three stages. Water is heated to between 60 C and the boiling point in a vessel fitted with an agitator and copperas is added until the overall concentration of ferrous sulphate is within the range $FeSO_4 : 7H_2O$ to $FeSO_4 : 9H_2O$. Additional copperas and, if necessary, water is added to maintain the concentration, whilst the suspension is agitated and the temperature kept within the required range. Part of the suspension is discharged either intermittently or continuously to, preferably, a spray drier. That part of the suspension not passed to the drier must be maintained within the temperature range and agitated to prevent solidification.

At a higher temperature (80 C) it has proved possible to prepare a slurry with concentrations between $FeSO_4 : 7H_2O$ to $FeSO_4 : 7.35H_2O$ whilst still retaining ease of agitation and when poured the slurry is smooth and homogeneous.

The spray drier used to dry a number of five kilo batches had a diameter of eight feet and an evaporative capacity of about 80 lbs. per hour. The inlet temperature of the air was 350 C and the outlet temperature 180 C. Slurry as obtained from the preferred method was fed at a rate of 218 lbs./hour and two samples of the dried product analysed $FeSO_4 : 1.4H_2O$ and $FeSO_4 : 1.6H_2O$, well within the required tolerance limits.

The spray dried product so obtained may be used by itself or with pyrites as a source of sulphur for the generation of gases containing SO_2 for sulphuric acid manufacture.

Development of this process is of considerable importance to all acid manufacturers who have large supplies of copperas themselves or access to them, as in the case of British Titan Products Co. Ltd. Although still in its early stages utilization of copperas by this method will undoubtedly appeal to many operators and thus provide yet another practicable source of by-product sulphur.

REMOVAL OF H_2S FROM GAS USING AN ORGANIC OXYGEN CARRIER

Summary

FOLLOWING SOME YEARS of experience with a small pilot plant incorporating an organic oxygen carrier for the removal of hydrogen sulphide, the Gas Council have begun construction of a 10,000 cu. ft. per hour plant. The first stage of this is now complete and the process has operated successfully at 200 cu. ft. per hour. The basic idea is not new, but the work reported here has aimed at the development of a process of practical value.

At total pressures of several atmospheres the partial pressure of hydrogen sulphide is so much greater than the partial pressure of water vapour at the operating temperatures that the water formed by the reaction cannot be carried forward in the gas stream.

The high-pressure process as at present envisaged consists in washing the fuel gas, which may contain a high percentage (up to at least 30%) of carbon dioxide, with a solution of an appropriate organic dyestuff in a suitable solvent. The hydrogen sulphide is oxidized to water and elemental sulphur. As the reaction is not reversible, complete removal can be obtained. The sulphur passes into solution and can be recovered in crystalline form by cooling the solution to a temperature

lower than that in the absorption tower. The cooled solution is warmed, and re-oxidized by free oxygen ready for re-use. The system as employed for high-pressure operation is not wholly suitable for working at near atmospheric pressure, but experiments have been made with a simple modification which may enable operation at atmospheric pressure to be achieved.

Features to be desired in a Purification Process

1. Avoidance of the handling of solid materials.
2. Ability to remove hydrogen sulphide completely.
3. Recovery of the sulphur in a convenient form.
4. Regeneration of the absorbent solution with the minimum use of steam or power.
5. The avoidance of air and water pollution, either by liquid or gaseous substances.

Organic Dyestuffs as Oxygen Carriers

It has long been thought that the maximum realisation of the desirable features in a hydrogen sulphide removal process would be attained if there were available an oxygen carrier performing a function similar to that performed by the haemoglobin of the human bloodstream. Such a substance could be employed in its reduced form to absorb oxygen in a vessel which would be the analogue of the lung, and, in its oxidized form, to part with that oxygen to the hydrogen sulphide which is to be removed.

In 1921 E. V. Evans and H. Stanier conducted an exhaustive examination of certain classes of organic dyestuffs which might be expected to behave in this manner and found that, while with many of them the oxidation reaction went smoothly, the reduction reaction was much slower. Amongst the few suitable was methylene blue, a dyestuff readily available commercially.

Water is one of the products of oxidation of hydrogen sulphide, and if the solvent chosen for the methylene blue has a limited solvent power for water there will separate from the solution of reduced dyestuff an aqueous layer. If, then, the aqueous layer be rendered alkaline with, for example, ammonia, acid radicals are removed as ammonium salts and these ammonium salts are removed from the system by draining off the aqueous layer.

The Choice of a Solvent

Pyridine and homologues were used as solvents for methylene blue in original work, but following extensive tests on over 600 solvents which possessed the necessary properties, aniline was finally chosen as a suitable, but by no means the only possible solvent: it lacks two advantages of the ideal solvent, it is corrosive to mild steel and consequently the vessels, pipelines and pumps in the pilot equipment were fabricated in stainless steel. Further it is toxic both as liquid and vapour, but a hazard recognised from the start can, with suitable precautions, be a hazard eliminated.

Side Reactions

Several kinds of reaction which might have wrecked the proposal were examined under conditions where these reactions were most likely to appear, and steps were taken to bring them under control.

1. *Formation of Sulphur Oxy-Acids.* When attempting to oxidize hydrogen sulphide to elemental sulphur, not all the sulphur is recovered in the elemental form, and a proportion appears as sulphur oxy-acids (thionates, thio-sulphate, sulphite or sulphate). The nuisance which they cause is considerable as, apart from the loss of saleable sulphur, the acid radicals combine with alkaline constituents of the washing medium, demanding separation and replacement, and can form the basis of a troublesome effluent problem. It has proved possible to operate the methylene blue process so as to keep the formation of sulphur oxy-acids to a low figure and then to introduce a simple operation for removing the small quantity which is formed. Sulphur oxy-acids are most readily formed if unoxidized hydrogen sulphide is allowed to remain in solution in the washing medium as it leaves the absorber, or if free oxygen remains in solution when the washing liquid returns to the absorber. Therefore, the plant is so operated that the washing liquid leaves the absorber with a substantial proportion of the blue still unreduced, and leaves the oxidizer for return to the absorber with a substantial proportion of the leuco compound still not re-oxidized, and thus the loss of sulphur as sulphur oxy-acids is kept well below 3% of

the total sulphur removed. An effective method of plant control over the degree of oxidation of the washing solution has been developed by applying the observation that the electrical conductivity of the solution changes with change in state of oxidation.

The sulphur which is oxidised to sulphur oxy-acids appears mostly in the form of sulphate, probably because of the strongly oxidizing action of the methylene blue. As mentioned earlier, the sulphate radical attaches itself to the methylene blue base and is removed, when the base is in the leuco form, by reaction with a solution of ammonium hydroxide. The ammonium sulphate is removed in comparatively strong solution (15%).

2. *Reaction with Hydrogen Cyanide.* If the gas to be purified contains hydrogen cyanide, some 90% of this impurity is removed and fixed as thiocyanic acid, which behaves in the same way as the sulphur oxy-acids already mentioned, and can be removed in a similar manner. This provides a convenient way of removing hydrogen cyanide from the gas, the cost of removal being substantially the cost of an equivalent amount of alkali

3. *Reaction with Organic Sulphur Compounds.* No reaction would be expected, nor has any been observed, between the solution and thiophene or carbon-oxysulphide, but, carbon disulphide is known to react slowly with aniline to form thiocarbanilide. The formation of thiocarbanilide is accelerated in the presence of an acceptor for the hydrogen sulphide liberated in the reaction, and methylene blue is such an acceptor. Therefore, if the gas contains carbon disulphide, that impurity will be removed and fixed as thiocarbanilide which, in turn, will leave the system as crystals mixed with the crystals of sulphur. There may be circumstances in which this method of carbon disulphide removal is attractive, but the recovery of aniline from thiocarbanilide is not a simple operation, and it is likely that in most cases it will be preferred to remove the carbon disulphide by oil washing for the reasons mentioned in the succeeding paragraph.

4. *Reaction with Certain Hydrocarbons.* Gases containing certain unsaturated hydrocarbons can give rise to pitch-like materials which increase the viscosity of the washing medium through the combination of these unsaturated hydrocarbons with the solution. The main offenders are the di-olefines which are known to cause trouble in other aspects of gas treatment and distribution. The steps to be taken to avoid trouble from this source are simple, particularly when the gas is under pressure, as they involve only the washing of the gas with gas oil or other suitable solvent which will remove these hydrocarbons and with them the carbon disulphide.

5. *Oxidation of Aniline.* When the examination of possible solvents showed aniline to possess the desired combination of qualities, there was considerable doubt about its stability in the presence of free oxygen, particularly if that oxygen were made in a bomb calorimeter where a small quantity of aniline in the presence of methylene blue and sulphur was exposed to a large excess of pure oxygen at 25 atm. pressure and at temperatures up to 50° C. No sign of oxidation of change of weight was found. Nevertheless, it has been thought prudent in the design of the plant to guard against any possible consequences which might result if aniline and oxygen did unexpectedly and, contrary to experimental evidence, react.

In the three years of operating experience with this process, no other complicating side reactions have been observed, nor has there been any reason to suspect that such reactions may take place.

Process Flow Diagrams

The process employing methylene blue is at present visualised in two forms; one working with gas at a pressure of several atmospheres, and the other treating gas at near atmospheric pressure.

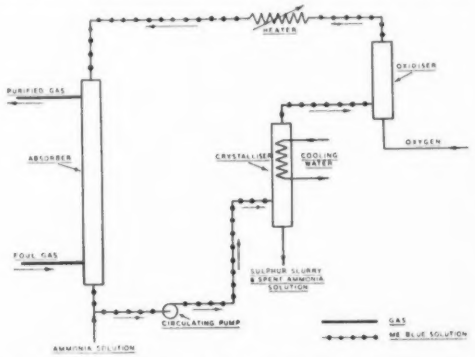


Fig. 13. Flow diagram of process for gas at high pressure

1. *High Pressure.* Losses of aniline vapour can easily be kept to a low level and removal of reactive pitch-forming hydrocarbons and carbon disulphide by oil requires only a small oil washer.

Three vessels and three operations are involved. In the absorber the hydrogen sulphide is removed from the foul gas and oxidized, the sulphur going into solution At the outlet of the absorber, ammonia solution is added to ensure the removal of any acid radicals that may have been formed, and the mixture of reduced solution plus aqueous ammonia passes to the crystalliser. Here the solution is cooled, and from the bottom of the crystalliser both sulphur slurry and an aqueous solution of ammonium salts are removed. The washing solution then passes from the top of the crystalliser to the oxidiser, where free oxygen is added and the solution is regenerated before being warmed and passed back to the absorber.

2. *Low Pressure.* At atmospheric pressure, the oil washer needs to be of considerable size and the loss of aniline as vapour is great enough to demand a solvent-recovery stage. In order to avoid these complications, the low-pressure system is visualised as comprising

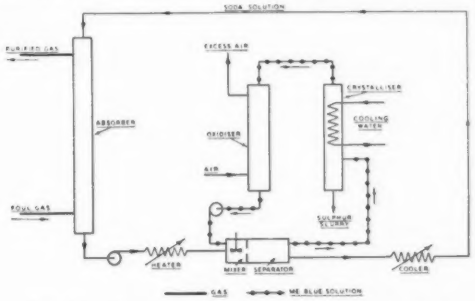


Fig. 14. Flow diagram of process for gas at near atmospheric pressure.

two circuits. In the first, an alkaline aqueous solution comes in contact with the gas and removes the hydrogen sulphide as the hydrosulphide of the dissolved alkali. The fouled solution is regenerated by stirring with a solution of methylene blue in aniline, when the hydrosulphide is completely oxidized and the aqueous solution returns to the gas scrubber free from hydrogen sulphide. The experimental work has shown that the gas can be purified to the statutory limit by this regenerated solution because regeneration is complete and not limited by equilibrium considerations. The aniline solution which has been mixed with the aqueous solution in order to regenerate the latter is separated, cooled to cause the dissolved sulphur to crystallise, and re-oxidized by air.

Pilot Plant

The first pilot plant, which has now been operated intermittently under a variety of conditions for some three years, was designed to purify up to 200 cu. ft. of gas/hr. at a pressure of 300lb./sq. in. As no supply of high-pressure gas was available, town gas was taken from the public supply, hydrogen sulphide was added, and the mixture was compressed, cooled, and washed with gas oil for the removal of pitch-forming hydrocarbons and carbon disulphide. In those experiments which were made to determine the effect of the presence of carbon dioxide, this gas was added under pressure at the outlet of the oil washer. The presence of 30 to 40% of carbon dioxide in the gas made no measureable difference to the absorption rate. Various types of absorber were tested, and the most successful were the plate-type and the ring-packed type. The concentration of hydrogen sulphide normally present in crude coal gas and any gasification gases is of the order of 10^2. The test which is carried out to ensure that town gas complies with the statutory requirements can detect a concentration of 10^6. The problem, therefore, is to reduce the concentration of hydrogen sulphide in the ratio of 10^4. To provide a safety margin, it is as well to design the plant to give an extraction equivalent to a reduction of 10^5 or 10^6, in which case, if the design performance is maintained in practice, the gas will contain 0.1 of 0.01 of the quantity permitted by the official test. For design purposes, therefore, the basic factor to be determined by experimental measurement is the number of plates or the height of packed column needed to reduce the hydrogen sulphide concentration in the ratio of 10^1. It was found that three sieve plates were sufficient to give this reduction in hydrogen sulphide concentration, and in consequence 12 plates should suffice for a reduction of 10^4 and 18 plates would give ample margin by giving a reduction in the ratio 10^6, or a concentration of hydrogen sulphide in purified gas of only 1 part/100 mill. The performance of a plate column is easier to predict when the scale is increased

than is the performance of a ring-packed column. A 2in. dia. column packed with $\frac{1}{8}$in. Raschig rings to a depth of 6ft. reduced the hydrogen sulphide concentration in the ratio 10^4 at a gas velocity of 200 cu. ft./hr. This result represents an absorption coefficient of 0.0038lb./hr./sq. ft. of surface, but attempts to scale up on these results have indicated the difficulty of predicting the effective wetted surface in such a column when both the size of the column and the size of rings are to be changed.

The second vessel of the circuit is the crystallizer, and for the small pilot plant this consisted of a tube 2in. dia. by 4ft. long fitted with a water jacket. The fouled solution passed slowly upwards through this tube, the velocity being limited to 0.1 ft./sec., and a bed of sulphur crystals was maintained within that tube. The heat transfer coefficient was only about 25 B.t.u./sq. ft./° F/hr. The purpose of the bed of sulphur crystals was to induce the sulphur coming out of solution to deposit on these crystals surfaces and so avoid fouling the heat transfer surface. With no bed of crystals, the sulphur coming out of solution did deposit on the cooled metal surface. This principle of carrying out cooling in the presence of sulphur crystals has proved so successful that it will be followed in the design of the larger unit, but the arrangement of head transfer surfaces must necessarily be different and the increase in scale may enable a higher heat transfer rate to be obtained. The removal at each passage of the solution of the sulphur which has been taken up during that passage requires a fall of temperature between the absorber and the crystallizer. The lower the rate of heat transfer, the greater this temperature change must be. In the small pilot plant, the absorber was operated at 90° to 100° F, and in the crystallizer the solution was cooled by about 10° F.

The slurry of crystalline sulphur is run off periodically from the base of the crystallizer. After filtration, the filter cake contains 85% of sulphur, the remainder being aniline/methylene blue solution trapped between the crystal surfaces. Washing with water is sufficient to displace the aniline solution and yield sulphur of 99% purity. Actually, a final wash with dilute hydrochloric acid is given because, bearing in mind the toxic nature of aniline vapour, it is desired to fix as hydrochloride any traces of aniline which may remain. The sulphur, although so high in purity, retains a greenish colour due to the presence of small quantities of the blue dyestuff.

The reaction between the reduced dyestuff and free oxygen is rapid and the practical factor limiting the speed of re-oxidation of the circulating liquid to the desired extent, using only a small proportion of excess oxygen. This is fortunate because, from the point of view of safety, it is desirable that there should be the minimum quantity of oxygen in contact with aniline at any one time. In the small pilot plant, as it has been worked, and in the projected larger plant, the amount of oxygen in contact with aniline can be so limited that, if the whole of it were unexpectedly to react simultaneously with the aniline present, it cannot raise the temperature more than a few °C. In the small pilot plant, the oxidation was

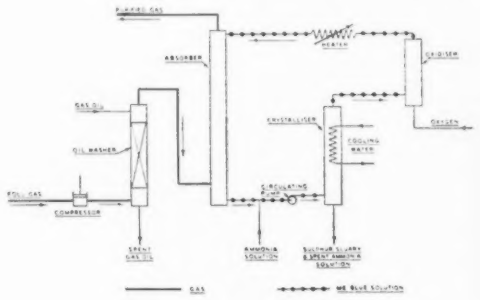


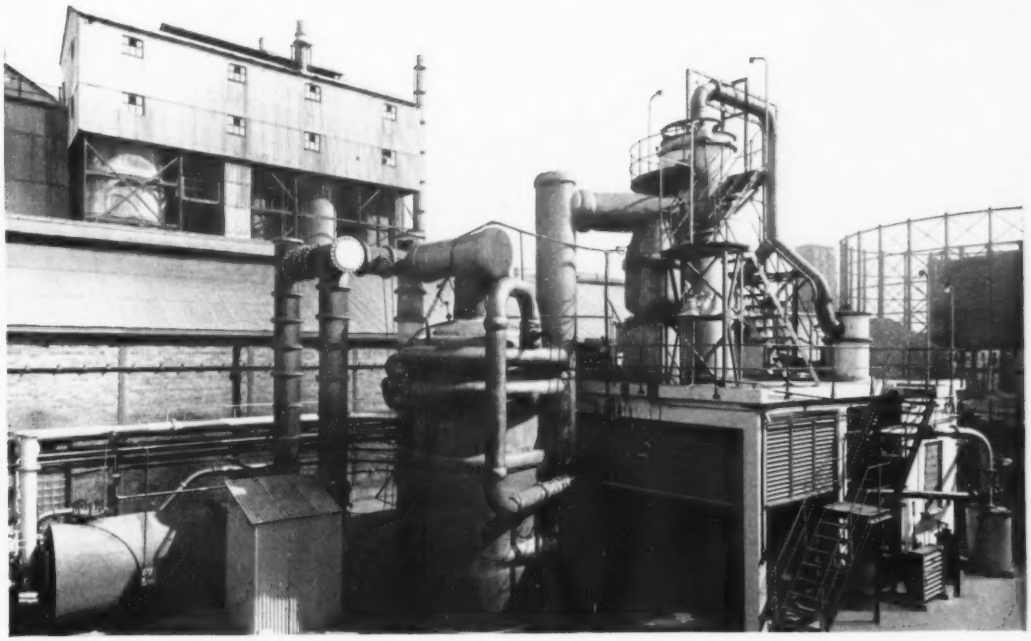
Fig. 15

carried out in a ring-packed flooded tower, the small oxygen bubbles finding their way up through the aniline and between the packing. Here again, it is not simple to scale up this design of plant, and for the larger semi-scale plant it is proposed to use a coil of pipe through which oxygen and the solution will pass in concurrent turbulent flow. The whole of this coil can be immersed in a tank of warm water, thereby enabling it to serve as a heat exchanger for rewarming the solution after crystallization as well as for carrying out the oxidation reaction.

The larger semi-scale plant for treating 10,000 cu. ft. of gas/hr. is now under construction and Figure 15 shows diagrammatically its arrangement.

WET CONTACT PLANTS

for sulphuric acid production from hydrogen sulphide



Wet contact plants are an efficient and economical means of producing sulphuric acid from H_2S gas, which may be derived from ammonium sulphate saturators or from liquid purification of coal gas.

In the latest Huntington Heberlein plants, maintenance costs are reduced by using acid-irrigated towers and mist precipitation equipment for the acid condensation in place of the tubular condensers of earlier plants, and capital cost is reduced by replacing the electro-precipitators formerly used for acid mist precipitation by simple mechanical ceramic tube filters. These features are incorporated in the plant shown, which was recently built at the Birmingham works of Brotherton & Co. Ltd., to produce 10 to 12 tons per day of 78 per cent sulphuric acid.

In suitable cases a waste heat boiler may be used as a gas cooler between the H_2S combustion chamber and the convertor.

Wet contact sulphuric acid plants by

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